

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Production of Polymers and Detergent Compounds therefrom

We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800 North Lindbergh Boulevard, St. Louis, 66, State of Missouri, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the production of polymers and particularly to a process for the polymerization of olefin hydrocarbons. More particularly, the present invention relates to a process for polymerizing normally gaseous mono-olefin hydrocarbons to produce olefin polymers of 8 to 16 carbon atoms, which olefin polymers, when used to provide the alkyl substituent in the production of alkylaromatic sulfonates afford alkylaromatic sulfonates of increased susceptibility to biological decomposition. The invention accordingly further relates to the production of alkylaromatic sulfonate detergent compounds from the said polymers.

Among the most widely used of the synthetic detergents are the alkylaromatic sulfonates. Usually these alkylaromatic sulfonate detergents derive their alkyl substituents from olefin hydrocarbons produced by the polymerization of lower molecular weight olefin hydrocarbons. Generally, the alkylaromatic sulfonates so produced possess relatively good functional properties from the detergent standpoint. However, these compounds are resistant to biological decomposition to such a degree that they are creating a substantial problem. Considerable amounts of detergent compound pass through sewage or waste disposal plants unchanged and when passed into lakes or streams are responsible for unsightly nuisances in the form of foam and scum and

also represent potential toxicity hazards to aquatic life and to communities down-stream.

Numerous catalysts and processes are available for the polymerization of olefin hydrocarbons to produce olefinic polymers of the proper molecular weight for inclusion in alkylaromatic sulfonates. However, few of these catalysts or processes have been found to produce olefin polymers which when used to provide the alkyl moiety in alkylaromatic sulfonates produce detergent compositions susceptible to biological decomposition. In our copending Application No. 28610/64 Serial No 1050379 there is described the production of novel catalysts which comprise activated carbon impregnated with an oxide of cobalt and activated by heating in a non-oxidising atmosphere at 400—575° C. As therein described the said catalysts are of particular value in the polymerization of olefinic hydrocarbons. The present invention makes use of the same catalysts for the polymerisation of olefinic compounds and is thus an improvement in or modification of the invention described and claimed in the said Application No. 28610/64.

According to the present invention there is provided a process for preparing an olefin fraction suitable for the preparation of biodegradable alkyl aromatic compounds, said process comprising polymerising in a first polymerisation zone normally gaseous mono-olefin hydrocarbons in the presence of an activated carbon supported cobalt oxide catalyst activated at a temperature of 200 to 350° C to form a polymer fraction, thereby to obtain a polymer fraction comprising dimers of the normally gaseous mono-olefin hydrocarbons, said dimers being of 4 to 8 carbon atoms and being to the extent of at least 85% by weight straight-chained dimers or branched-chain dimers containing only a single sub-

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stituent, contacting said dimer fraction in a second polymerisation zone at elevated temperature with an activated carbon supported cobalt oxide catalyst activated at a temperature of 400 to 575° C to form a second polymer fraction, separating said second polymer fraction to obtain a fraction comprised of mono-olefin dimers of the olefin hydrocarbons in the feed to the second polymerisation zone, said dimers being of 8 to 16 carbon atoms.

According more specifically to the present invention there is provided a process for preparing an olefin fraction suitable for the preparation of biodegradable alkyl aromatic compounds which comprises contacting in a first polymerisation zone normally gaseous mono-olefin hydrocarbons at a temperature of 0 to 200° C and a pressure of atmospheric to 2500 psig, with an activated carbon supported cobalt oxide catalyst activated at a temperature of 200 to 350° C, to form a polymer fraction, separating said polymer fraction to obtain a fraction comprising dimers of the normally gaseous mono-olefin hydrocarbons, said dimers being of 4 to 8 carbon atoms and being to the extent of at least 85% by weight straight chained dimers or branched chain dimers containing only a single substituent, contacting said dimer fraction in a second polymerization zone at a temperature of 50 to 250° C and a pressure of atmospheric to 2500 psig, with an activated carbon supported cobalt oxide catalyst activated at a temperature of 400 to 575° C to form a second polymer fraction, separating said second polymer fraction to obtain a fraction comprised of non-olefin dimers of the olefin hydrocarbons in the feed to the second polymerization zone, said dimers being of 8 to 16 carbon atoms. This relatively linear mono-olefin dimer fraction of mono-olefin hydrocarbons of 8 to 16 carbon atoms, when reacted with an aromatic compound to form an alkylaromatic compound produces an alkylaromatic compound of increased susceptibility to biological decomposition.

Though the above embodiment suggests the use of the olefin dimer fraction of 8 to 16 carbon atoms in the alkylation of an aromatic compound for the ultimate production of an alkylaromatic sulfonate, the present invention is not to be so severely limited. This olefin fraction may be used in the preparation of any detergent composition which requires an alkyl substituent of 8 to 16 carbon atoms. For example, the olefin fraction is useful in the preparation of alkyl sulfonates in which the alkyl group is directly connected to the sulfonate radical or in which the alkyl group is connected to the sulfonate radical by an intermediate linkage such as an ester, ether, amide, or like groups. Also, this olefin fraction is useful in preparing alkylaromatic sulfonates in which the alkyl group is

joined to the aromatic nucleus through intermediate linkages such as ester, ether, amide and like groups. This olefin fraction comprised of mono-olefin hydrocarbons of 8 to 16 carbon atoms produced by the present invention finds further utility in the preparation of alkanols and other like uses wherein relatively linear olefins are particularly useful.

The term "dimer" as used herein, refers to those polymers obtained by the condensation of two and only two molecules or monomer units of mono-olefinic hydrocarbons. These molecules or monomer units may be like or unlike. For example, dodecenes produced by the condensation of two hexene-1 molecules or the condensation of a butene-1 molecule and an octene-1 molecule are equally within the meaning of the term "dimer" as used herein.

For purposes of simplifying the description of the present invention, the polymerization of normally gaseous mono-olefin hydrocarbons, briefly described above, will be hereinafter referred to as the "first stage dimerization" and the dimer product obtained from this first stage dimerization as the "first stage dimer." The polymerization of the first stage dimer, also briefly described above, is hereinafter referred to as the "second stage dimerization" and the dimer product obtained from this second stage dimerization as the "second stage dimer."

The base supports useful in the catalysts used in both the first and second stage dimerizations are activated carbons. These activated carbons may be any porous carbon known to be useful for catalyst preparation. The activated carbons generally have surface areas of about 400 to 2000 square metres per gram and may be in the form of compact masses, granules, chips, powders, etc. Suitable supports include coconut charcoal, wood charcoal, carbon derived from coke, soft bone charcoal, hard bone charcoal, and the like. The activated carbon may be obtained from animal, vegetable or petroleum sources and may include such commercial materials as Pittsburgh "BPL", "CAL", "OL" and "SGL" produced by Pittsburgh Coke and Chemical Co., Girdler "G-32-C", and "G-32-E" produced by Chemical Products Division, Chemetron Corp., and Barnebey-Cheney Company's "EE-1" and "E-H-1".

In preparing the activated carbon supported cobalt oxide dimerization catalysts for both the first and second stage dimerizations, an activated carbon is impregnated with a solution of a cobalt salt and the salt subsequently converted to the oxide. This treatment of the activated carbon may be carried out by immersion of the carbon in the cobalt salt solution, by just moistening the carbon with the cobalt salt solution or by any other means known to those skilled in the art for impregnation of catalyst supports. The cobalt salt solution consists of a cobalt salt dissolved

in any suitable solvent for the cobalt salt. Generally, wherever practical, aqueous or alcoholic solutions of the cobalt salt are used. Among the cobalt salts useful for impregnation of the activated carbon are the following non-limiting examples: Cobalt acetate, cobalt sulfate, cobalt nitrate, cobalt butanoate, cobalt pentanoate, cobalt hexanoate, cobalt chromate, cobalt vanadate, cobalt molybdate, cobalt iodate, cobalt oxalate, cobalt citrate, cobalt sulfite and the like. The most useful cobalt salts are cobalt acetate, cobalt sulfate and cobalt nitrate in the cobaltous form with cobalt nitrate being the preferred salt. The cobalt salt solution is preferably an aqueous solution having a concentration calculated to give the desired amount of cobalt oxide on the activated carbon after activation of the catalyst.

Prior to treatment of the activated carbon with a cobalt salt solution, the activated carbon may be acid washed or base treated or both prior to impregnation with a cobalt salt. If the activated carbon is to be acid washed, aqueous nitric acid will most often be used as the acid. This aqueous nitric acid is preferably used in an amount of approximately 1 to 2 volumes of acid per volume of activated carbon e.g. 600 to 1000 ml of acid per 500 ml of activated carbon. Generally, when using an acid wash, the concentration of the acid is preferably 10 to 30% by weight in water. The acid wash, when used, will generally be from 2 to 10 minutes in duration with 3 to 5 minutes generally being sufficient. After acid washing, the activated carbon is washed with water and if desired, dried.

In addition to or in place of acid washing, it is in many instances preferred to pretreat the activated carbon with a non-oxidizing gas or liquid. Usually, it is preferred that the activated carbon be dried previous to this form of pretreatment. When treating the activated carbon with a non-oxidizing gas, the gas is merely passed over the activated carbon, generally at a temperature of 150 to 500° C for 0.5 to 8 hours. It is preferred that the non-oxidizing gases include such gases as hydrogen, nitrogen, ammonia, helium, and argon. These non-oxidizing gases may be used alone or in combination. It is preferred that the non-oxidizing gas, if used, be one selected from the group consisting of hydrogen, nitrogen, ammonia and combinations thereof with ammonia being preferred over the others. The non-oxidizing gases, when used, will generally be in the gaseous state; however, it is within the scope of the present invention to use the non-oxidizing gases in a liquefied form. Thus, in referring to these non-oxidizing gases as gases, it is meant that they are normally gaseous and not that they are limited to utilization in the gaseous form.

Among the non-oxidizing liquids which may

be utilized in this pretreatment of the activated carbon are such compounds as ammonium hydroxide and the like. In most instances, the preferred non-oxidizing liquid is ammonium hydroxide. The non-oxidizing liquid is used in practically any concentration and the treatment carried out by immersing the dried activated carbon in the non-oxidizing liquid for a time sufficient for complete adsorption by the activated carbon of the maximum amount of the liquid adsorbable by the carbon. In using the preferred non-oxidizing liquid, ammonium hydroxide, concentrations of 15 to 30% by weight in water preferably will be used. Generally, treatment of the activated carbon with a non-oxidizing liquid is at ambient temperatures (20 to 40° C) though both higher and lower temperatures may be used.

The particularly preferred manner of treating the activated carbon prior to impregnation with cobalt salt is referred to as "ammoniation" and consists of pretreating the carbon with either ammonia or ammonium hydroxide or a combination thereof as described in the preceding paragraph. When both ammonia and ammonium hydroxide are used it is immaterial whether one or the other is used first followed by the other or whether they are used simultaneously.

Though not necessary, it generally is desirable to have the activated carbon dry before it is treated with the cobalt salt solution. A particularly useful, but by no means limiting manner of drying the activated carbon, comprises heating the activated carbon at a temperature of 50 to 200° C for 2 to 24 hours. A preferred method of drying the activated carbon comprises maintaining the carbon at a temperature of 100 to 150° C for 2 to 6 hours. To facilitate drying, reduced pressures may be used. Of course, reduced pressures will shorten the drying period and/or lower the temperatures.

After the activated carbon has been impregnated with the cobalt salt solution, the impregnated activated carbon is generally subjected to a drying treatment. This drying treatment is carried out in the manner described in the preceding paragraph. It is not absolutely necessary that the catalyst be completely dried prior to activation. However, caution should be exercised in activating a catalyst which has not been subjected to at least partial drying. The drying step after impregnation brings about decomposition of the cobalt salt. Thus, if the catalyst has not been subjected to drying, there is a distinct possibility of over rapid decomposition resulting in an explosion when the catalyst is directly subjected to activation.

The most critical feature in the preparation of the activated carbon supported cobalt oxide catalysts of the present invention is in the activation conditions of the catalysts. The

catalyst which is used in the first stage dimerization, generally, is activated at a temperature of 200 to 350° C. The preferred activation temperature for this first stage dimerization catalyst is 225 to 300° C. Activation of the activated carbon supported cobalt oxide catalyst used in the second stage dimerization is most often carried out at temperatures within the range of 400 to 575° C with temperatures of 425 to 525° C being preferred. Generally, a period of 0.25 to 3 hours is sufficient for complete activation of the catalyst, whether it is the first or second stage dimerization catalyst. The catalyst activation is carried out in the presence of an inert atmosphere. Several non-limiting examples of inert atmospheres in which the catalysts may be activated are nitrogen, carbon dioxide, propane, helium, argon, and the like. As a practical matter, nitrogen usually is preferred as the inert atmosphere. Activation may be carried out at slightly reduced pressures if desired. When reduced pressures are used, it is preferred from a practical standpoint that the pressure not be reduced below 10 mm. Hg., though lower pressures may be used.

Another factor of some importance in the dimerization catalysts, both for the first and second stage dimerizations, is the amount of cobalt, present as cobalt oxide, on the finished catalyst. The first stage dimerization catalyst usually contains from 2 to 30 percent by weight of cobalt, as cobalt oxide. With this first stage dimerization catalyst, however, optimum results are obtained with cobalt concentrations toward the lower end of this range. Therefore, lower concentrations of cobalt, as cobalt oxide, are preferred, these lower concentrations being within the range of 8 to 15 percent by weight of cobalt, as cobalt oxide. With the second stage dimerization catalyst, it has been found that there is a less apparent criticality in the concentration of cobalt present in the catalyst. However, there seems to be some benefit in using higher concentrations of cobalt, as an oxide, in the second stage dimerization. Therefore, though the second stage dimerization catalyst may contain 2 to 50 percent by weight and higher of cobalt, as an oxide, it is generally preferable to use a second stage dimerization catalyst having a cobalt concentration, as an oxide, within the range of 5 to 30 percent by weight of the total catalyst. Preferably, for optimum dimerization activity, the cobalt, as cobalt oxide, is present in the second stage dimerization catalyst in an amount equivalent to 12 to 30 percent by weight of the finished catalyst.

The first stage dimerization step of the present process dimerizes normally gaseous mono-olefin hydrocarbons. The normally gaseous mono-olefin hydrocarbons are ethylene, propylene and butylenes. The feed to the

first stage dimerization may contain only one of these mono-olefins or it may contain a mixture of two or more. When two or more of these mono-olefins are present both dimerization and co-dimerization will take place. For example, if the feed comprises ethylene and propylene, then ethylene dimers of 4 carbons and propylene dimers of 6 carbon atoms will be formed as well as will be formed ethylene-propylene co-dimers of 5 carbon atoms. If the normally gaseous mono-olefin feed includes butylenes, it is usually preferred that the butylenes be *n*-butylenes. Further, it is preferred that the *n*-butylene be terminally unsaturated. The preferred feed to the first stage dimerization is propylene. Though it is generally preferred to have a relatively pure normally gaseous mono-olefin hydrocarbon feed to the first stage dimerization, it is not altogether necessary. The feed may contain small amounts of mono-olefins other than the normally gaseous mono-olefins. However, since the primary purpose of the first stage dimerization is to produce dimers of 4 to 8 carbon atoms, the amount of other polymerizable mono-olefins present in the feed should be kept to a minimum. The presence of diolefins and triolefins as well as acetylenic compounds in the feed is to be avoided since these materials poison the catalyst to some extent. Preferably, the feed will contain no greater than approximately 0.002% by weight of polyolefins. Saturated hydrocarbons as well as other inert materials may be present in the feed to a considerable extent. Such materials have no deleterious effect on the dimerization reaction. However, as a practical matter, large quantities of these materials are to be avoided since they are merely "dead weight" to the process and needlessly increase the cost of handling the feed materials and products.

The feeds to the second stage dimerization reaction are the mono-olefinic dimer products of the first stage dimerization. These dimer products are of 4 to 8 carbon atoms depending upon the normally gaseous mono-olefin hydrocarbons in the feed to the first stage dimerization. If the preferred normally gaseous mono-olefin hydrocarbon, propylene, is the feed to the first stage dimerization, then the dimer feed to the second stage dimerization is ordinarily of 6 carbon atoms. A particularly preferred mono-olefin dimer feed to the second stage dimerization is one which contains no greater than 10% by weight of branched-chain mono-olefin hydrocarbons with the remainder of the mono-olefins being straight-chain. The mono-olefin hydrocarbons in the feed to the second stage dimerization include both internally and terminally unsaturated mono-olefin hydrocarbons. Since the feed to the second stage dimerization is a product of the first stage dimerization, there will generally be fewer impurities such as

diolefins, triolefins, saturated hydrocarbons, inert materials and the like than are in the feed to the first stage dimerization. Further, since in most instances the product from the first stage dimerization is subjected to a separation step to recover the dimers produced and to exclude excess branched-chain mono-olefins, most of the impurities such as those above mentioned may, if present, also be removed during this separation step.

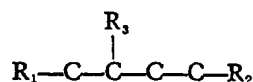
The separation step used for purifying the product of the first stage dimerization to meet the above discussed feed requirements of the second stage dimerization may be carried out by any conventional means. Generally, ordinary fractional distillation will be adequate for effecting the purification of the dimer product of the first stage dimerization. The determination of the precise fractionation equipment and conditions for obtaining the second stage dimerization feed, is well within the ability of those skilled in the art having the above definition of this feed before them. When the preferred feed, propylene, is dimerized in the first stage dimerization, fractionation of the dimer product to obtain an overhead fraction having a boiling range of approximately 60 to 75° C will usually provide a suitable feed for the second stage dimerization. In addition to or in place of fractional distillation, other conventional separation or purification means such as adsorbents, i.e., molecular sieves, solvent extraction, extractive distillation, selective polymerization, isomerization and the like may be employed to conform the dimer product of the first stage dimerization to the feed requirements of the second stage dimerization. To repeat, it is immaterial to the present invention what separation means is used for purifying the product of the first stage dimerization to meet the feed requirements of the second stage dimerization, so long as such separation means provides the desired purification.

One of the primary advantages found in the herein disclosed first stage dimerization process is found in its production of relatively large quantities of dimers meeting the above defined feed requirements to the second stage dimerization. The amount of second stage dimerization feedstock produced by the first stage dimerization is significantly improved over other conventional processes. To meet the above defined second stage feed requirements, it is generally necessary to remove a portion of the branched-chain dimers by such means as fractionation. Many of the isomeric branched-chain dimers are exceptionally difficult to separate from the straight-chain dimers by ordinary separation means such as fractionation. The first stage dimerization process of the present invention produces significantly less of these difficultly separable branched-chain isomers than do other known polymerization processes.

In carrying out the first stage dimerization, temperatures within the range of 0 to 200° C are generally used. Preferably, however, the temperatures are within the range of 50 to 150° C. The temperatures of the second stage dimerization overlap those of the first stage dimerization, but are usually somewhat higher. The most useful temperatures for the second stage dimerization are within the range of from approximately 50 to 250° C. However, second stage dimerization temperatures of 100 to 175° C are preferred. Dimerization pressures in both the first and second stage dimerizations usually are within the range of from approximately atmospheric pressure to 2500 psig and higher. Preferably, however, the first stage dimerization pressures will be within the range of from 50 to 750 psig with pressures of 100 to 500 being still more preferred. Pressures for the second stage dimerization will usually be somewhat lower and most often will be within the range of from approximately 10 to 400 psig with pressures of 100 to 300 psig being preferred.

Both the first and second stage dimerizations may be carried out batchwise or as a continuous process. As a practical matter, the dimerization reactions most often will be carried out as continuous processes with the feed material passed continuously over an activated carbon supported cobalt oxide catalyst bed and the dimer continuously recovered as effluent from the catalyst bed. The space velocity of the feed material in the catalyst zone usually is within the range of 0.1 to 50 liquid volumes of feed per hour per volume of catalyst. Preferred space velocities for the first stage dimerization reaction are within the range of from 1 to 50 liquid volumes of feed per hour per volume of catalyst. The preferred space velocities for the second stage dimerization reaction are within the range of from 0.1 to 5 liquid volumes of feed per hour per volume of catalyst.

The polymer product obtained from the second stage dimerization is comprised of dimers of the feed mono-olefins and also some higher molecular weight polymers. This polymer product is subjected to fractional distillation or to some other separation means to recover the total dimer fraction from the unpolymerized feed material and the polymers of higher molecular weight than dimers, i.e., trimers, tetramers, etc. The dimer product of this second stage dimerization generally contains 90 to 95% by weight of dimers which are straight-chained or branched-chain containing a single substituent. Upon hydrogenation these dimers have the general saturated formula



wherein the total number of carbon atoms is 8 to 16 and wherein R_1 and R_2 may be hydrogen or a n -alkyl hydrocarbon group of 4 to 12 carbon atoms and R_3 may be hydrogen or a n -alkyl hydrocarbon group selected from the group consisting of methyl, ethyl and propyl. The particularly preferred dimer product of the second stage dimerization is one in which the dimers are of 12 carbon atoms and which is comprised of 15 to 55% by weight of methyl undecenes and 25 to 85% by weight of n -dodecenes. This preferred product is generally obtained by using propylene as the feed to the first stage dimerization and then recovering from the first stage dimerization product the hereinabove discussed and defined preferred feed to the second stage dimerization.

The method whereby the product obtained from the second stage dimerization is separated to obtain the dimer fraction, is not critical to the present invention. Practically any method of separation may be used. It is only necessary that the separation means be such as to separate the relatively linear dimer fraction from the unpolymerized olefins of the feed and the polymers higher in molecular weight than the dimers.

According to a further feature of the present invention there is provided a process for the production of alkylaromatic sulfonates susceptible to biological decomposition which comprises reacting the relatively linear dimers of 8 to 16 carbon atoms obtained in the second stage dimerization of the foregoing two-stage process, with an aromatic compound in the presence of an alkylation catalyst under alkylating conditions to form an alkyl aromatic compound, sulfonating said alkyl aromatic compound and subsequently neutralizing the alkyl aromatic sulfonate.

In this further feature of the invention, after the dimer fraction is obtained from the second stage dimerization, it is reacted under alkylation conditions with an aromatic compound to form an alkyl aromatic compound. This alkylation reaction may be carried out by any of the methods known to the art. The process by which alkylation of the aromatic compound with the dimer is carried out may include those using such catalysts as the Friedel Crafts type catalysts such as $AlCl_3$, $GaCl_3$, $FeCl_3$, $TiCl_4$, $SnCl_4$, $ZnCl_2$, and the like as well as such other alkylation catalysts as HF , H_2SO_4 , H_3PO_4 , on Kieselguhr. Alkylation in the presence of Friedel-Crafts type catalysts will most often be carried out in presence of a hydrogen halide, i.e., HCl , HBr , HI , HF . The catalyst and hydrogen halide will usually be present in a weight ratio of 2:1 to 1:2. The alkylation also may be carried out by purely thermal alkylation means. Alkylation conditions include temperatures ranging from 0 to 425° C and with, of course, higher temperatures being necessary for ther-

mal alkylation. Also, elevated pressures may be utilized, especially in thermal alkylation which often uses pressures in excess of 1000 psig. Of course, the amount of catalyst, as well as the relative amounts of aromatic and dimer fractions, will vary considerably depending on catalyst and process conditions. Preferably, the mol ratio of dimer fraction to aromatics will be 0.5:1 to 5:1 though other ratios may be used. A very practical and somewhat preferred manner of carrying out the alkylation of the aromatic compounds is that illustrated by the examples hereinafter presented. Briefly described, this preferred mode of alkylating the aromatic compound with the second stage dimer comprises subjecting the dimer and aromatic compound in a mol ratio of 1:6 to a temperature of 30 to 35° C for 30 to 60 minutes in the presence of a Friedel-Crafts type catalyst, particularly aluminum chloride, and a hydrogen halide, preferably HCl , the ratio of catalyst to hydrogen halide being 1:1. It is, of course, understood that this merely represents a preferred and practical method of alkylation and is in no manner to be construed as limiting the present invention.

The aromatic compounds which may be alkylated with the mono-olefin dimer fraction in the practice of the present invention includes any of the aromatic compounds known and conventionally utilized in the preparation of detergent compositions. These aromatic compounds include aromatic hydrocarbons, both mono- and poly-nuclear. The aromatic hydrocarbons are both substituted and unsubstituted aromatics. When substituted, the aromatic nucleus may have any number of substituents, though it is usually preferred that there be no more than two substituents already on the aromatic nucleus. The substituents to the aromatic nucleus may be any substituent which will not appreciably interfere with the surface activity of the finished alkyl aromatic sulfonate. Generally, it is preferred that the aromatic nucleus have no more than two alkyl substituents and that these substituents have no more than 3 carbon atoms per substituent. Among the aromatic hydrocarbons which may be alkylated with the mono-olefin dimer fraction in the preparation of biodegradable alkyl aromatic sulfonates, for detergent use are the following non-limiting examples: benzene, toluene, ethylbenzene, xylenes, iso-propyl benzene, n -butyl benzene, diethylbenzenes, naphthalene, methylnaphthalenes, dimethylnaphthalenes, ethylnaphthalenes, diethylnaphthalenes, diphenyl, methyldiphenyl, dimethyldiphenyls, ethyldiphenyls, anthracene, phenanthrene, methylphenanthrene, methylanthracene, dimethylantracene, diethylphenanthrene and the like. The particularly preferred aromatic hydrocarbons for the purposes of the present invention are benzene, toluene, naphthalene and methyl naphthalenes. In

addition to the aromatic hydrocarbons, such other aromatic compounds as those in the following non-limiting list may be made to produce more biodegradable detergents by incorporation thereon of the present mono-olefin dimer fraction as an alkyl substituent. These aromatic compounds include phenols, cresols, xlenols, lower alkylated phenols, phenol ethers, diaryl ethers, naphthols, naphthol ethers, phenyl phenols and the like.

The sulfonation of the alkyl aromatic hydrocarbon may be accomplished by any number of methods. Useful methods include those wherein the sulfonating agents are sulfuric acid, anhydrous sulfur trioxide, chlorosulfonic acid or such special reagents as sulfuric acid-acetic anhydride, sulfur trioxide-pyridine, sulfur trioxide-dioxane and the like. Generally, it would be preferred to use sulfuric acid of a strength of 10 to 80%. The sulfonating agents generally are used in a molar equivalent to the alkyl aromatics being sulfonated. However, if desired, an excess of sulfonating agent may be used. Sulfonation may be carried out at temperatures ranging from 20° C and lower up to 60° C and higher. After sulfonation is complete, the product is neutralized with an alkali. A very practical and somewhat preferred method of sulfonating the alkyl aromatic compound is that illustrated by the example hereinafter presented. This somewhat preferred method comprises treating the alkyl aromatic compound for 5 to 7 minutes with 20% oleum at a temperature of 47 to 53° C while maintaining vigorous agitation, thereafter lowering the temperature to 37 to 43° C for about 40 to 50 minutes and adding water and subsequently recovering the sulfonic acid layer and thereafter neutralizing with an alkali solution, particularly sodium hydroxide. This method is only a preferred method and is in no manner limiting to the present invention.

The following examples will serve to illustrate the various aspects of the present invention.

EXAMPLE I

Approximately 86.5 grams of a commercial grade (BPL) activated carbon was immersed in approximately 52.4 grams of cobalt nitrate hexahydrate dissolved in 90 mls. of demineralized water. Excess water was removed and the impregnated carbon dried at a low heat for approximately 2 hours until there was no visible liquid on the catalyst mass. The catalyst was then placed under vacuum at 125° C for 16 hours and then activated in the presence of nitrogen at 35 mm. Hg. and a temperature of 275° C for 2 hours. The amount of cobalt, as oxide, present in this catalyst was approximately 13.5% by weight of the catalyst.

Approximately 27 grams of the above prepared catalyst was placed in an one inch

diameter stainless steel cylinder four inches in length. A propylene stream comprised of 83 weight percent propylene and 17 weight percent propane was then passed through the catalyst bed at a space velocity of 1.4 grams of feed per gram of catalyst per hour. The catalyst bed was maintained at a temperature of approximately 50° C and a pressure of 720 psig. The product was collected and subjected to fractionation to obtain a dimer fraction having a boiling range of 61 to 75° C. This dimer fraction represented 50% by weight of the polymer product and had the following composition:

Component	Weight Percent	
Hexene-1	10	80
<i>trans</i> -Hexene-3	8	
<i>cis</i> -Hexene-3	2	
<i>trans</i> -Hexene-2	52	
<i>cis</i> -Hexene-2	21	85
2-Methylpentene-1	6	
2-Methylpentene-2	1	

This first stage dimer fraction represents the feed stock to the second stage dimerization.

A second catalyst was prepared in the same manner as that described above with the exception that the catalyst was activated at a temperature of approximately 475° C and in the presence of nitrogen for 3 hours. The amount of cobalt, as an oxide present in the catalyst, was approximately 13.5% by weight of the total catalyst.

Approximately 80 grams of this catalyst were placed in a cylindrical reactor of the same dimensions as described above. Approximately 79 grams of the fraction whose composition is set out above was passed through this catalyst bed at a rate of 120 mls. per hour. The catalyst bed was maintained at a temperature of approximately 150° C and at a pressure of approximately 300 psig. The product was subjected to distillation and a dimer fraction having a boiling range of 38 to 100° C at 30 mm. Hg. was obtained. This dimer fraction represented 90% by weight of the polymer product and had the following composition:

Component	Weight Percent	
<i>n</i> -dodocenes	29.9	115
methyl undecenes	43.1	
ethyl decenes	27.0	

In order to demonstrate the efficacy of the present invention, the relatively linear dimer fraction prepared in the second stage dimerization in the above example was used for the alkylation of benzene which was subsequently sulfonated to an alkylbenzene sulfonate. The alkylbenzene sulfonate was then tested for its biodegradability by comparison with an

extensively used conventional alkylbenzene sulfonate which is one in which the alkyl substituent is derived from the tetramerization of propylene over a phosphoric acid catalyst by the process disclosed in U.S. patent No. 2,075,433.

Alkylation was carried out by placing approximately 175.5 grams of dry benzene in a cylindrical glass reactor equipped with a cooling coil thermometer well and means for agitation. Next, anhydrous hydrogen chloride was bubbled into the reactor for approximately 7 minutes. To this mixture was added approximately 3.2 grams of anhydrous aluminum chloride. Next, approximately 100 grams of the above described C_{12} dimer fraction was added over a period of 15 minutes to the benzene catalyst mixture. Continuous agitation was maintained throughout the addition of the olefin material and the temperature was maintained between 30 to 35° C throughout this period. After completion of the addition of the olefin, the reaction mass was allowed to age for approximately 15 minutes. The alkylation mass was then allowed to settle without agitation for one hour and the lower catalyst complex layer separated from the reaction mass. The remaining alkylated liquor was then washed with an equal volume of tap water.

Approximately 259 grams of the washed alkylated liquor was distilled batchwise through a 1/2 inch diameter packed column 12 inches in height. Benzene was recovered at atmospheric pressure at a 1:1 reflux ratio from the distillation. After removal of the benzene, the distillation was continued under reduced pressure. The alkylbenzene product cut was obtained within the boiling range of 123° C to 135° C at 2 mm. Hg. Approximately 83.7 grams of alkylbenzene was recovered.

Approximately 75 grams of the distilled alkylbenzenes were charged to a 250 ml. flask. To this was added approximately 105 grams of 20% oleum. The oleum was added over a 6-minute period while maintaining vigorous agitation and while maintaining a temperature of $50 \pm 3^\circ$ C. After the addition of the oleum was complete the temperature was lowered to $40 \pm 3^\circ$ C and held for approximately 45 minutes. To this mixture was then added approximately 16.5 mls. of distilled water at such a rate that the temperature of the mixture could be held below 65° C. After the water was added, addition was stopped and the sulfonation mass transferred to a centrifuge tube and centrifuged for 30 minutes. The lower spent acid layer was separated and the sulfonic acid layer dissolved in 750 mls. of 80% isopropanol. The solution was then neutralized to a pH of 7.0 to 9.0 with a 25% sodium hydroxide solution. The resultant mixture was filtered to remove solid Na_2SO_4 and the remaining solution dried to obtain alkylbenzene sulfonate.

To test the alkylbenzene sulfonate so prepared for its biodegradability, two tests were used. The first of these tests was "activated sludge test". The second test was the "river water test". These tests and the results obtained therefrom are described below.

The activated sludge test is carried out by contacting the test compounds with a sludge obtained from an activated sludge sewage disposal plant in the following manner. Approximately 1500 mls. of the sludge was maintained at room temperature and normal room lighting conditions in a 2 liter graduate while under constant agitation by a stream of air introduced near the bottom of the graduate for approximately 23 hours. The sludge was allowed to settle for one hour and then 1000 mls. of the supernatant liquor was withdrawn and replaced by one liter of tap water containing 25 milligrams of test compound, 150 mgs. of Glucose, 159 mgs. of nutrient broth, 150 mgs. of sodium benzoate, 150 mgs. dipotassium hydrogen phosphate and 25 mgs. ammonium sulfate. The aeration was then continued for the next 23 hours and once more allowed to settle and then 1000 mls. of the supernatant liquid decanted. The decanted liquid is analyzed for test compound by the Longwell-Maniece modification of the methylene blue method as described in *The Analyst*, Vol. 82, 826-827, (1957). The amount of test alkylbenzene sulfonate in the decanted effluent was subtracted from the amount initially added to obtain the amount of test material which had biodegraded. From this the percent biodegradation of the test compounds was obtained. For greater accuracy in this procedure, the tests were repeated over and over until a constant percent biodegradation was obtained for each test compound. The results of the tests are given in the following table wherein alkylbenzene sulfonate A is one prepared from the C_{12} dimer product of the Example and alkylbenzene sulfonate B is the conventional propylene tetramer derived alkylbenzene sulfonate.

	% Biodegradable	
Alkylbenzene sulfonate A	96	
Alkylbenzene sulfonate B	62	115

The second test used, the river water test, is a comparative test and as such is indicative of the relative rates of biological decomposition of any number of different compounds being tested. The specific river water used is not critical, but due to the variance of type of bacteria in river water and the day-to-day differences in bacterial concentration, portions of the same river water sample should be used for all comparison tests. The river water test comprises mixing 5 to 10 parts per million of alkylbenzene sulfonates with a very dilute culture of soil organisms contained in a sample

of river water, and then periodically determining the alkylbenzene sulfonate content of the river water. The concentration of alkylbenzene sulfonate in the river water is determined by the methylene blue test, which comprises introducing methylene blue into a sample of the alkylbenzene sulfonate containing river water, thereby producing a salt of the alkylbenzene sulfonate with the methylene blue. This salt is then extracted with an organic solvent such as chloroform and the solution color measured. The methylene blue analysis used herein is described in *The Analyst*, Vol. 62, 826—827, (1957). The rate and amount of the reduction of concentration of alkylbenzene sulfonate in the mixture is a comparative measure of its susceptibility or, conversely, resistance to bacterial attack.

A sample of river water was obtained and separated into two equal portions, each in

a separate vessel. To one of these portions was added an amount of the alkylbenzene sulfonate A from the C₁₂ dimer prepared in accordance with the present invention sufficient to bring about a concentration of 7.0 parts per million of the alkylbenzene sulfonate in the river water. To the other portion of the river water was added alkylbenzene sulfonate B prepared from the propylene tetramer obtained from the conventional phosphoric acid polymerization of propylene. The amount of this conventional dodecylbenzene sulfonate added was sufficient to bring about a concentration of 8.4 parts per million of the conventional dodecylbenzene sulfonate in the river water. The concentration of the alkylbenzene sulfonate in the river water was then determined at 0, 10, 20 and 28 days. The following table summarizes the data thus obtained.

		Concentration in ppm			
		0 days	10 days	20 days	28 days
Alkylbenzene Sulfonate A		6.7	1.7	0.2	0.1
Alkylbenzene Sulfonate B		8.7	5.5	2.2	2.2

EXAMPLE 2

To approximately 300 grams of a commercial grade (BPL) activated carbon was added approximately 300 mls. of concentrated ammonium hydroxide. All of the ammonium hydroxide was adsorbed. The ammonium hydroxide treated activated carbon was dried for approximately two hours at about 130° C. Next, the dried carbon was immersed in a solution of approximately 200 grams of cobalt nitrate hexahydrate in 250 mls. of demineralized water. The cobalt nitrate impregnated carbon was then dried at a low heat for approximately 3 hours until there was no visible liquid or water on the carbon and placed under vacuum for about 18 hours at a temperature of 120° C. The dried cobalt nitrate impregnated carbon was immersed in approximately 500 mls. of concentrated ammonium hydroxide which was rapidly absorbed. This catalyst was then dried to visible dryness and placed under vacuum at 120° C for 25 hours. As a final step, the catalyst was activated by heating at a temperature of 275° C in the presence of a nitrogen flow for 3 hours. This catalyst contained approximately 13.6% by weight of cobalt, calculated as cobalt oxide.

Approximately 27 grams of the above prepared catalyst were placed in a one inch diameter stainless steel cylinder four inches in length. A propylene stream comprised of 83 weight percent propylene and 17 weight percent propane was then passed through the catalyst bed at a space velocity of 1.2 to 1.3 grams of feed per gram of catalyst per hour. The catalyst bed was maintained at a temperature of approximately 50° C and a

pressure of 750 psig. A polymer fraction representing a conversion of 50% was collected and subjected to fractionation from which a dimer fraction having a boiling range of 61 to 75° C was obtained. This dimer fraction had the following composition:

Component	Weight Percent
Hexene-1	10
<i>trans</i> -Hexene-3	8
<i>cis</i> -Hexene-3	2
<i>trans</i> -Hexene-2	52
<i>cis</i> -Hexene-2	21
2-Methylpentene-1	6
2-Methylpentene-2	1

This dimer fraction represents the feedstock to the second stage dimerization.

A second catalyst was prepared in the same manner as that described above with the exception that the catalyst was activated at a temperature of approximately 475° C for 2 hours in the presence of nitrogen. The catalyst contained approximately 13.5% by weight of cobalt, as an oxide.

Approximately 56.2 grams of this catalyst were placed in a reactor of the same dimensions as described above. Approximately 3,926 grams of the fraction whose composition is set out above was passed through this catalyst bed at a rate of 0.67 mls. per minute. The catalyst bed was maintained at a temperature of approximately 150° C and at a pressure of approximately 300 psig. The polymer fraction recovered was subjected to distillation and approximately 251 grams of dodecenes were obtained.

Alkylation was carried out by placing approximately 175.5 grams of dry benzene in a cylindrical glass reactor equipped with a cooling coil thermometer well and means for agitation. Next, anhydrous hydrogen chloride was bubbled into the reactor for approximately 7 minutes. To this mixture was added approximately 3.2 grams of anhydrous aluminum chloride. Next, approximately 100 grams of the above described C₁₂ dimer fraction was added over a period of 15 minutes to the benzene-catalyst mixture. Continuous agitation was maintained throughout the addition of the olefin material and the temperature was maintained between 30—35° C throughout this period. After completion of the addition of the olefin, the reaction mass was allowed to age for approximately 15 minutes. The alkylation mass was then allowed to settle without agitation for one hour and the lower catalyst complex layer separated from the reaction mass. The remaining alkylated liquor was then washed with an equal volume of tap water.

Approximately 259 grams of the washed alkylated liquor was distilled batchwise through a 1/2 inch diameter packed column 12 inches in height. Benzene was recovered at atmospheric pressure at a 1:1 reflux ratio from the distillation. After removal of the benzene, the distillation was continued under reduced pressure. The alkylbenzene product fraction was obtained within the boiling range of 123° C to 135° C at 2 mm. Hg. Approximately 83.7 grams of alkylbenzene was recovered.

Approximately 75 grams of the distilled alkylbenzenes were charged to a 250 ml. flask. To this was added approximately 105 grams of 20% oleum. The oleum was added over a 6-minute period while maintaining vigorous agitation and while maintaining a temperature of 50±3° C. After the addition of the oleum was complete the temperature was lowered to 40±3° C and held for approximately 45 minutes. To this mixture was then added approximately 16.5 mls. of distilled water at such a rate that the temperature of the mixture could be held below 65° C. After the water was added, alkylation was stopped and the sulfonation mass transferred to a centrifuge tube and centrifuged for 30 minutes. The lower spent acid layer was separated

and the sulfonic acid layer dissolved in 750 mols. of 80% iso-propanol. The solution was then neutralized to a pH of 7.0 to 9.0 with a 25% sodium hydroxide solution. The resultant mixture was filtered to remove solid Na₂SO₄ and the remaining solution dried to obtain alkylbenzene sulfonate.

In order to demonstrate the efficacy of the alkylbenzene sulfonate prepared in accordance with the present invention it was compared in biodegradability with a conventional alkylbenzene sulfonate. The conventional alkylbenzene sulfonate used as a standard is that most extensively used in present day detergents which is an alkylbenzene sulfonate prepared from propylene tetramer. The propylene tetramer was obtained by the commonly used process for polymerizing propylene which is the polymerization of propylene over a phosphoric acid catalyst as set out in U.S. Patent No. 2,075,433. The method for preparing an alkylbenzene sulfonate from the tetramer was substantially the same as the alkylation and sulfonation procedures set out above. In comparing the conventionally prepared propylene tetramer derived alkylbenzene sulfonates with an alkylbenzene sulfonate prepared in accordance with the present invention, the "activated sludge test" described in Example I was used. The results of the tests are given in the following table wherein alkylbenzene sulfonate A is one prepared in accordance with the present invention and alkylbenzene sulfonate B is the one prepared from the conventional propylene tetramer.

	%
Alkylbenzene Sulfonate A	96
Alkylbenzene Sulfonate B	62

Consideration of the above example clearly demonstrates the efficacy of the present invention.

To further illustrate the biodegradability of the alkylbenzene sulfonate prepared in accordance with the present invention, a sample of the conventional tetramer derived alkylbenzene sulfonate described in the preceding example was compared with the present alkylbenzenes by the "river water test" described in Example I.

The following table summarizes the data thus obtained.

	Concentration in ppm				
	0 days	7 days	14 days	21 days	28 days
Alkylbenzene Sulfonate A	6.7	2.0	0.4	0.24	0.13
Alkylbenzene Sulfonate B	8.7	5.5	5.5	2.1	2.34

The present invention is further exemplified by an alkylbenzene sulfonate prepared from a C₁₂ olefin fraction obtained by using a catalyst system wherein the catalyst used in the first stage dimerization is the same as

that described in Example 2, but wherein the catalyst used in the second stage dimerization is prepared as follows: An activated carbon is impregnated with a salt of cobalt, dried and thereafter activated at a temperature

of approximately 475° C. The olefin fraction was obtained by the polymerization of propylene in a first stage dimerization to form a polymer product which was separated to obtain a dimer fraction. This dimer fraction was subjected to polymerization in a second stage dimerization to form a second dimer fraction which was then used to alkylate benzene. The alkylbenzene so obtained was sulfonated and neutralized to obtain an alkylbenzene sulfonate. The alkylbenzene sulfonate so obtained is substantially more biodegradable than the conventional dodecylbenzene sulfonate described above.

The present invention is further illustrated by other alkyl aromatic compounds such as naphthalenes, mixed xylenes, ortho-xylene, meta-xylene, para-xylene, ethylbenzene, methylnaphthalene, ethylnaphthalene, and dimethylnaphthalene, and particularly by the preparation of an alkyl aromatic sulfonate using as the aromatic hydrocarbon, toluene. The alkyl aromatic sulfonates so prepared are significantly more susceptible to biological decomposition than are similar conventional alkyl aromatic compounds.

WHAT WE CLAIM IS:—

1. A process for preparing an olefin fraction suitable for the preparation of biodegradable alkyl aromatic compounds, said process comprising polymerising in a first polymerisation zone normally gaseous mono-olefin hydrocarbons in the presence of an activated carbon supported cobalt oxide catalyst activated at a temperature of 200 to 350° C to form a polymer fraction, thereby to obtain a polymer fraction comprising dimers of the normally gaseous mono-olefin hydrocarbons, said dimers being of 4 to 8 carbon atoms and being to the extent of at least 85% by weight straight-chained dimers or branched-chain dimers containing only a single substituent, contacting said dimer fraction in a second polymerisation zone at elevated temperature with an activated carbon supported cobalt oxide catalyst activated at a temperature of 400 to 575° C to form a second polymer fraction, separating said second polymer fraction to obtain a fraction comprised of mono-olefin dimers of the olefin hydrocarbons in the feed to the second polymerisation zone, said dimers being of 8 to 16 carbon atoms.
2. A process for preparing an olefin fraction suitable for the preparation of biodegradable alkyl aromatic compounds, said process comprising contacting in a first polymerisation zone normally gaseous mono-olefin hydrocarbons at a temperature of 0 to 200° C and a pressure of atmospheric to 2500 psig with an activated carbon supported cobalt oxide catalyst activated at a temperature of 200 to 350° C to form a polymer fraction, separating said polymer fraction to obtain a fraction comprising dimers of the normally gaseous mono-olefin hydrocarbons, said dimers being of 4 to 8 carbon atoms, and being to the extent of at least 85% by weight straight-chained dimers or branched-chain dimers containing only a single substituent, contacting said dimer fraction in a second polymerisation zone at a temperature of 50 to 250° C and a pressure of atmospheric to 2500 psig with an activated carbon supported cobalt oxide catalyst activated at a temperature of 400 to 575° C to form a second polymer fraction, separating said second polymer fraction to obtain a fraction comprised of mono-olefin dimers of the olefin hydrocarbons in the feed to the second polymerisation zone, said dimers being of 8 to 16 carbon atoms.
3. A process according to claim 1 or 2 wherein the said dimers of 8 to 16 carbon atoms comprise at least 90% by weight of straight-chain dimers and/or branched-chain dimers containing only a single substituent.
4. A process according to any of claims 1—3 wherein the first catalyst is activated at a temperature of 225 to 300° C.
5. A process according to any of claims 1—4 wherein the second catalyst is activated at a temperature of 425 to 525° C.
6. A process according to any of claims 1—5 wherein the normally gaseous mono-olefin is propylene.
7. A process according to any of claims 1—6 wherein the first polymerisation zone is maintained at a temperature of 50 to 150° C and a pressure of 50 to 750 psig.
8. A process according to any of claims 1—7 wherein the second polymerisation zone is maintained at a temperature of 100 to 175° C and a pressure of 10 to 400 psig.
9. A process according to any of claims 1—8 wherein both catalysts are activated in a non-oxidising atmosphere.
10. A process according to claim 9 wherein the non-oxidising atmosphere is selected from propane carbon dioxide, helium, argon and mixtures thereof.
11. A process according to claim 9 wherein the non-oxidising atmosphere is nitrogen.
12. A process according to any of claims 1—11 wherein the first polymerisation zone is maintained at a temperature of 50 to 150° C and a pressure of 100 to 750 psig, and wherein the second polymerisation zone is maintained at a temperature of 100 to 175° C and a pressure of 100 to 300 psig.
13. A process according to claim 1 substantially as hereinbefore described with reference to either of the foregoing specific Examples.
14. An olefin fraction when prepared or produced by any of the processes hereinbefore described and claimed in any of claims 1—13.
15. A process for the preparation of alkyl aromatic sulfonates susceptible to biological decomposition, which comprises reacting an olefin fraction prepared by any of the pro-

- cesses claimed in claims 1—13 with an aromatic compound in the presence of an alkylation catalyst under alkylation conditions to form an alkyl aromatic compound, sulfonating said alkyl aromatic compound and neutralising the alkyl aromatic sulfonate thus formed.
- 5 16. A process according to claim 15 wherein the aromatic compound is benzene or naphthalene.
- 10 17. A process according to claim 15 substantially as hereinbefore described with reference to either of the foregoing specific Examples 1 and 2.
18. Alkyl aromatic sulfonates whenever prepared or produced by any of the processes of claims 15 to 17.

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